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(54) Title: LIQUID DUROPLASTICS

(57) Abstract: Reinforced liquid duroplastics are prepared by adding to the duroplastics a pyrogenically prepared silica which has been surface-modified with silanes containing methacrylic groups.



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Liquid duroplastics

The invention relates to a method of reinforcing liquid duroplastics, and to the resulting duroplastics.

5 Duroplastics refers to all plastics produced from curable resins. According to DIN 7724, up to the decomposition temperature they are crosslinked, close-meshed, highly polymeric materials, which are steel-elastic at lower temperatures and behave elastically with very limited
10 deformability between 50°C or a higher temperature and the decomposition temperature. The shear modulus does not fall below 10^2 kp/cm² at any temperature.

Duroplastics are generally amorphous. As a result of the crosslinking of the duroplastics, their molecules are
15 unable to conduct any macro-Brownian movements. Micro-Brownian movements of the polymer molecules, on the other hand, are possible at the glass transition temperatures, which are above 50°C.

The term duroplastics is identical with the designation
20 duromer, which is sometimes preferred because it is more closely connected in terms of form with elastomers and plastomers (thermoplastics) as designations for the two other classes of plastics.

Duroplastics are widely used as moulding compositions,
25 cast resins, resin adhesives and lacquer resins. The duroplastics include *inter alia* the commercially important groups of materials (abbreviations according to DIN 7728, P1, 1st January 1988, in brackets) of the diallyl phthalate resins (DAP), epoxy-melamine-formaldehyde
30 resins (MF), melamine-phenol-formaldehyde resins (MP), phenol-formaldehyde resins (PF) and unsaturated polyester resins (UP).

It is known to use pulverulent silica as a filler for polymers.

In general, the filler, finely distributed in the form of a hard phase surrounded by the softer polymer, improves a number of commercially valuable mechanical properties. These include hardness, tensile strength, stress values and other measurable properties.

In principle, a distinction must be made between thermoplastic polymers and crosslinkable polymers. Silica can be used as a filler in both classes of materials. However, the added amounts and the effects can be very different owing to the polymer.

It is also known to use silica as a thickener in liquid duroplastics. That is not the subject of this invention, however; rather, the thickening action of the silica should be as little as possible.

The present invention describes the use of a silica modified with unsaturated organic groups in low molecular weight, generally liquid, reactive polymers. It is shown that it is possible to achieve an advantageous combination of rheological properties and mechanical properties, namely low viscosity and low flow limit in the uncrosslinked state on the one hand, and high hardness and high modulus in the crosslinked state on the other hand.

It is known to treat fillers used in polymers with vinylsilane or methacrylic silanes in order to obtain advantageous properties in the crosslinked product. It is in accordance with the prior art to carry out such treatment during mixing of the filler into the polymer.

The disadvantage of that procedure is that the chemical reaction sequence necessary for the desired binding of the silane to the solid takes place in an environment that is difficult to control, and its reproducibility leaves something to be desired. Moreover, alcohols form as an

unavoidable waste product; alcohols are generally undesirable as constituents of the polymer material and must be removed in a complex operation.

5 The silanes themselves and the cleavage products formed therefrom are a source of risk in respect of combustibility and toxicity and often require additional safety measures and investment. It is therefore desirable to use a filler which already contains the desired reactive groups and does not release any undesirable
10 substances into the polymer or into the environment.

The invention provides a method of reinforcing liquid duroplastics, which method is characterised in that a mixture of the uncrosslinked resin and a pyrogenically prepared silica which has been surface-modified with
15 silanes containing methacrylic groups is prepared.

The invention also provides liquid duroplastics which are characterised in that they contain pyrogenically prepared silica which has been surface-modified with silanes containing methacrylic groups.

20 In a particular embodiment of the invention, the pyrogenically prepared silica may be structurally modified.

According to the present invention, a particularly effective filler is a silica which contains methacrylic
25 groups and has been prepared by flame hydrolysis and whose structure has been altered by mechanical after-treatment.

A pyrogenically prepared silica which can be used in accordance with the invention is characterised by:

30	BET surface area m ² /g	from 20 to 380
	particle size nm	from 6 to 110
	tamped density g/l	from 50 to 600
	pH value	from 3 to 10
	carbon content %	from 0.1 to 15
	DBP number %	<200

It can be prepared by intensively mixing a silica in a suitable mixing device first with water or dilute acid and then with the surface-modifying agent, or by applying a mixture of various surface-modifying agents by spraying.

5 The components are mixed further for a period of from 15 to 30 minutes and then subjected to heat treatment at a temperature of from 100 to 400°C over a period of from 1 to 6 hours.

In a preferred embodiment of the invention, a
10 pyrogenically prepared silica can be used as the silica.

Pyrogenic silicas are prepared by flame hydrolysis of volatile silicon compounds, such as, for example, SiCl_4 , methyltrichlorosilane or the like. They are known from Ullmann's Enzyklopädie der technischen Chemie 4th edition,
15 Volume 21, page 464 (1982).

In a preferred embodiment of the invention, a pyrogenic silica having a BET surface area of approximately 200 m²/g can be used.

As surface-modifying agents there may be used monomeric
20 substances, such as methacryloxypropyltrialkoxysilanes, in which alkoxy can mean methoxy, ethoxy and/or propoxy.

An essential feature of the mentioned invention is the linking of the filler with the reactive monomers and oligomers of the lacquer by photopolymerisation.

25 Surprisingly, it has been found that, with particular liquid resin systems, even in the absence of light, a silica which contains methacrylic groups and has been prepared by flame hydrolysis and whose structure has been altered by mechanical after-treatment yields
30 disproportionately hard polymers, which are distinguished by advantageous properties.

Examples of such resin systems are:

- Unsaturated polyester resins of various compositions:

A. ethylenically unsaturated polyesters

B. ethylenically unsaturated monomers copolymerised with
A,

5 C. from 5 to 300 wt.%, based on A+B, of fibrous
reinforcing agents,

D. optionally pulverulent fillers,

E. optionally from 0.5 to 5 wt.%, based on A+B, of
thickening agents,

10 F. from 0.5 to 5 wt.%, based on A+B, of organic
peroxides,

G. aromatic amines, metal salts of organic acids, e.g.
cobalt compounds,

H. optionally further conventional additives.

15 A. As unsaturated polyesters there are suitable the
conventional polycondensation products of polyvalent,
especially divalent, carboxylic acids and their
esterifiable derivatives, especially anhydrides, which
are linked in the manner of esters to polyhydric,
especially dihydric, alcohols, and optionally
20 additionally contain radicals of monohydric alcohols
and/or radicals of hydroxycarboxylic acids, wherein at
least some of the radicals must have ethylenically
unsaturated copolymerisable groups.

25 As polyhydric, especially dihydric, optionally
unsaturated alcohols there are suitable the
conventional alkanediols and oxaalkanediols having
acyclic or cyclic groups, such as, for example,
ethylene glycol, 1,2-propylene glycol, 1,3-
30 propanediol, 1,3-butylene glycol, 1,4-butanediol, 1,6-
hexanediol, 2,2-dimethylene-1,3-propanediol,
diethylene glycol, triethylene glycol, polyethylene

glycol, dipropylene glycol, 1,2-cyclohexanediol, 2,2-bis-(hydroxy-cyclohexyl)-propane, trimethylolpropane monoallyl ether or 1,4-butanediol.

- 5 It is also possible to use concomitantly subordinate amounts of mono-, tri- or higher-hydric alcohols, such as, for example, ethylenehexanol, fatty alcohols, benzyl alcohols, 1,2-di-(allyloxy)-propanol-(3), glycerol, pentaerythritol or trimethylolpropane. The
- 10 polyhydric, especially dihydric, alcohols are generally reacted in a stoichiometric amount with polybasic, especially dibasic, carboxylic acids or their condensable derivatives.
- 15 Suitable carboxylic acids and their derivatives are dibasic, olefinically unsaturated, preferably β -olefinically unsaturated, carboxylic acids, such as, for example, maleic acid, fumaric acid, chloromaleic acid, itaconic acid, methyleneglutaric acid and
- 20 mesaconic acid and their esters or, preferably, their anhydrides. It is also possible in addition for other dibasic, unsaturated and/or saturated as well as aromatic carboxylic acids having a modifying action to be condensed into the polyesters, such as, for
- 25 example, succinic acid, glutaric acid, methylglutaric acid, adipic acid, sebacic acid, pimelic acid, phthalic anhydride, o-phthalic acid, isophthalic acid, terephthalic acid, dihydrophthalic acid, tetrahydrophthalic acid, tetrachlorophthalic acid, 3,6-
- 30 endomethylene.1,2,3,6-tetrahydrophthalic acid, endomethylenetetrachlorophthalic acid or hexachloro-endomethylenetetrahydrophthalic acid, also mono-, tri- and higher-basic carboxylic acids, such as, for example, ethylhexanoic acid, fatty acids, methacrylic
- 35 acid, acrylic acid, propionic 1,2,4,5-benzene-tetracarboxylic acid. Maleic acid or its anhydride and fumaric acid are preferably used.

Unsaturated polyesters which have been prepared using dicyclopentadiene can also advantageously be used.

It is also possible to use mixtures of unsaturated polyesters, including those which have only limited solubility in the monomers B and which readily crystallise. Such readily crystallising unsaturated polyesters may be composed, for example, of fumaric acid, adipic acid, terephthalic acid, ethylene glycol, 1,4-butanediol, 1,6-hexanediol and neopentyl glycol.

The unsaturated polyesters have acid numbers of from 5 to 200, preferably from 20 to 85, and mean molecular weights of approximately from 800 to 6000, preferably from approximately 1000 to 4000.

The amorphous and optionally crystallisable unsaturated polyesters are generally prepared from their starting components by melt condensation under azeotropic conditions according to continuous or discontinuous processes.

B. Suitable copolymerisable, ethylenically unsaturated monomeric compounds are the allyl and, preferably, vinyl compounds conventionally used in the preparation of unsaturated polyester moulding compositions, for example vinyl aromatic compounds, such as styrene, methylenestyrene, p-chlorostyrene or vinyltoluene; esters of acrylic acid and methacrylic acid with alcohols having from 1 to 18 carbon atoms, such as methacrylic acid methyl ester, acrylic acid butyl ester, ethylhexyl acrylate, hydroxypropyl acrylate, dihydrodicyclopentadienyl acrylate, butanediol diacrylate and (meth)acrylic acid amides; allyl esters, such as diallyl phthalate, and vinyl esters, such as ethylhexanoic acid vinyl ester, vinyl acetate, vinyl propionate, vinyl pivalate and others. Also suitable are mixtures of the mentioned olefinically

unsaturated monomers. Preferably suitable as component B are styrene, vinyltoluene and diallyl phthalate. The monomers B are contained in the polyester moulding compositions generally in an amount of from 10 to 80 wt.%, preferably from 20 to 70 wt.%, based on the total weight of components A and B.

C. As reinforcing fibres there are suitable inorganic or organic fibres in the form of rovings or flat structures optionally woven therefrom, such as mats, for example of glass, carbon fibres, asbestos, cellulose and synthetic organic fibres, such as polycarboxylic acid esters, polycarbonates and polyamides. The reinforcing fibres are used in amounts of from 5 to 300 wt.%, preferably from 10 to 150 wt.%, based on components A+B.

D. Suitable fillers are, for example, conventional finely powdered or granular inorganic fillers, such as chalk, kaolin, quartz powder, dolomite, heavy spar, metal powder, aluminium hydrate, cement, talcum, kieselguhr, wood dust, wood shavings, pigments and the like. They are used in SMC moulding compositions in amounts of from 0 to 200 wt.%, in BMC moulding compositions in amounts of from 100 to 400 wt.%, based on A+B.

E. As thickeners there may be mentioned, for example, alkaline earth oxides or hydroxides, such as calcium oxide, calcium hydroxid, magnesium hydroxide and, preferably, magnesium oxide, as well as mixtures of their oxides or hydroxides. They may also be partially replaced by zinc oxide. Polyisocyanates or metal alcoholates are also suitable in some cases. The thickeners are added to the moulding compositions in amounts of from 0.5 to 5 wt.%, based on A+B.

F. As polymerisation initiators there are used conventional organic peroxides that generate free radicals at elevated temperature, in amounts of from

0.05 to 5 wt.%, preferably from 0.1 to 3 wt.%, based on the total weight of components A and B. Suitable initiators are, for example: benzoyl peroxide, tert-butyl peroctoate, tert-butyl perbenzoate, dicumyl peroxide, di-tert-dibutyl peroxide and perketals, such as, for example, trimethylcyclohexamonperketal, as well as percarbonates.

G. Further conventional additives are, for example, inhibitors, such as hydroquinone, 2,6-dimethylhydroquinone, tert-butylbenzocatechin, p-benzoquinone, chloranil, 2,6-dimethylquinone, nitrobenzenes, such as m-dinitrobenzene, thiodiphenylamine or salts of N-nitroso-N-cyclohexylhydroxylamine, as well as mixtures thereof. The inhibitors are contained in the moulding compositions generally in an amount of from 0.005 to 0.2 wt.%, preferably from 0.01 to 0.1 wt.%, based on components A+B.

As lubricants there come into consideration, for example, zinc, magnesium and calcium stearates as well as polyalkylene ether waxes.

Such polyester resins are known, for example, from EP 0 120 272 A1.

- Vinyl ester resins, the VE resins also referred to as phenacrylate resins (abbrev. PHA), are reaction resins based on phenyl(ene) derivatives, such as, for example, aromat. glycidyl ethers of phenols or epoxidised novolaks, whose mol. have been esterified by (meth)acrylic acid.

The so-called "vinyl ester" class of resins has for some years been recognized as useful for a wide range of resin applications, especially those demanding superior chemical resistance. The resins are chemically the reaction products of epoxy resins and ethylenically unsaturated

products of epoxy resins. Typical vinyl ester resins now commercially available include the EPOCRYL resins (marketed by Shell Chemical Company), DERKANE 411 (marketed by Dow Chemicals Company) and CO-REZYN VE-8300
5 (marketed by Itnerplastic Company).

In the use of vinyl ester resins to prepare shaped products, in particular fibreglass-reinforced plastic (FRP) structures, the viscosity of the resin composition should be controlled so that the composition is fluid
10 enough to allow easy application and good wetting of fillers and reinforcement, yet not so fluid that it drains from vertical surfaces to cause resin-starved areas in the shaped products. Moreover, in many uses, for instance where shaped products such as pipes, tanks, scrubbers or
15 ducts are prepared using a vinyl ester resin, excellent body and hold-up characteristics are very important if not critical to the procedure, especially during the shaping and curing steps. In such applications, the resin is typically dissolved in a vinyl monomer, e.g., styrene,
20 whereupon it is shaped cured to produce shaped products. If, during the shaping and curing steps, the body and hold-up characteristics of the composition are such that outflow or running of the composition occurs when, for instance, the resin composition is applied onto a vertical
25 surface for lining, the resin surface of the shaped product may be of uneven thickness and have diminished mechanical strength.

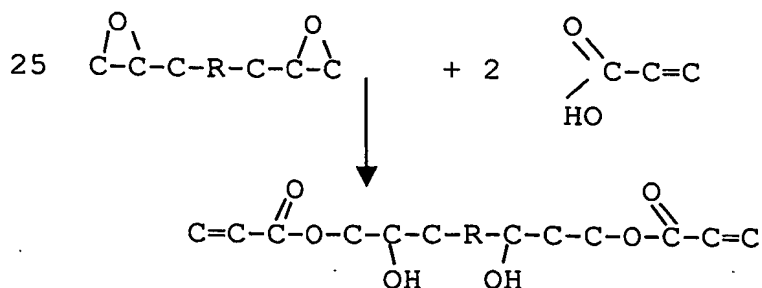
It has previously been proposed to improve the viscosity, body and hold-up characteristics of vinyl ester resins by
30 adding certain thixotropic agents. It has been reported that fumed silica are "extremely effective" thixotroping additives in certain vinyl ester resin compositions (see "Unsaturated Polyester Technology" edited by Paul F. Gruins; Gordon and Breach Science Publishers.

35 A composition of the present invention may comprise a comonomer, in order to facilitate handling, cure and to

provide desired mechanical properties. Suitable compatible comonomers include reactive, ethylenically unsaturated comonomers such as styrene, chlorostyrene, vinyltoluenes, methylstyrene, diallyl phthalate, triallyl cyanurate, acrylate esters, methacrylate esters and divinyl-benzene. Styrene is the preferred compatible adjuvant. The composition may also comprise a non-reactive diluent, such as acetone, where properties obtainable only with the neat resin are desired.

- 10 The vinyl ester resins used in the present invention may be any of those known in the art and may be prepared by an addition reaction between an epoxy resin and an ethylenically unsaturated monocarboxylic acid. Processes for preparing suitable vinyl ester resins are disclosed in
- 15 U.S. Patent Specifications Nos. 3,256,226; 3,317,465; 3,345,401; 3,373,221; 3,377,406; 3,432,478; 3,548,030; 3,564,074; 3,634,542 and 3,637,518.

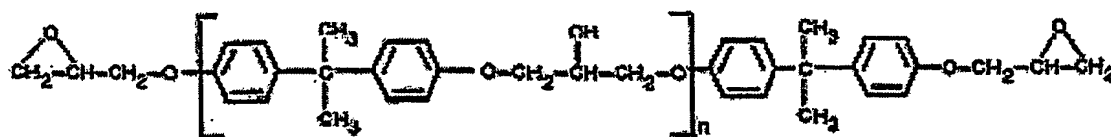
In general, the reaction by means of which the vinyl ester resins used in the present invention are prepared is straightforward. It may be catalysed by suitable catalysts such as, for instance, tertiary amines, phosphines, alkalis or onium salts. The general equation for the reaction may be represented as follows:



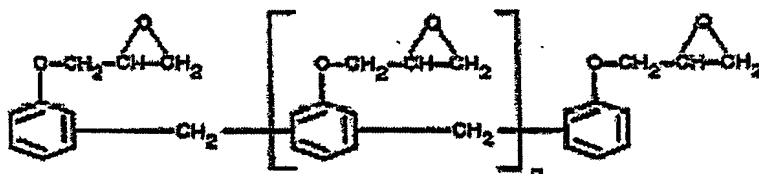
- 30 wherein R is, for instance, alkylene, cycloalkylene, arylene, arylalkylene, oxyarylene, oxyarylalkylene or cycloalkylene ester.

Suitable acids are acrylic, methacrylic, crotonic and cinnamic acids. Suitable epoxy resins are the following:

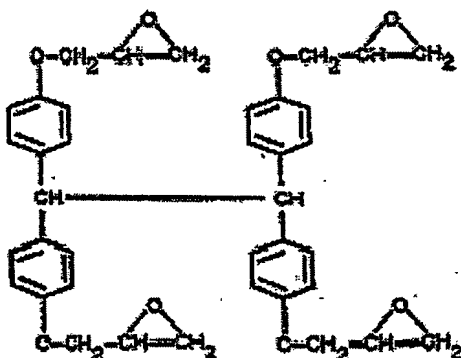
BPA Ерсу



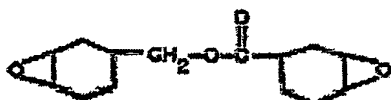
Epoxy Novolac



Tetraphenylethane Epoxy



Cycloaliphatic Epoxy



A substantial number of different vinyl esters combining different characteristics may be prepared by combining different epoxy resins with various unsaturated acids. The variety of products may of course be even further extended, depending upon the selection of the unsaturated monomers which can be combined, and copolymerised, with the vinyl ester resin. The vinyl ester resins which have so far achieved the greatest utility and which are therefore preferred for use in the present invention are the bisphenol-A (BPA)-epoxy based vinyl ester resins. These resins may be employed in the compositions of the present invention either with or without a co-reactive monomer such as styrene.

In addition to the vinyl ester resin, thixotroping additive and, if desired, a reactive or non-reactive diluent, the resin composition of the present invention may also comprise catalysts, inhibitors, fillers, pigments
5 and/or other known conventional additives.

Compositions of the invention may be polymerised and cross-linked, using free radical generating initiators which are known in the art. Polymerisation of the resin is by means of a true addition reaction and, typically, no
10 by-products are formed. Suitable initiators include peroxides, preferably organic peroxides such as benzoyl peroxides or methyl ethyl ketone peroxide, as well as other sources of free radicals. For example, photoinitiators which generate free radicals may also be
15 used to initiate polymerisation of the composition of the present invention. The initiator may be used with conventional accelerators or promoters such as, for instance, tertiary amines, e.g. dimethyl or diethyl aniline, and metallic soaps such as cobalt or manganese
20 octoate or naphthenate.

Various shaping methods may be employed to shape the resin composition. Suitable methods include the hand lay-up method, the coldpress method, the bag method, the matched-die method, the filament-winding method and the continuous
25 moulding method.

- Acrylic resins may be cold- or heat-curable synthetic resins, which are obtained by homopolymerisation of (meth)acrylic acid esters (so-called pure-A.) or their copolymerisation with, for example, styrene or
30 vinyl esters. Heat-curable acrylic resins additionally contain functional groups (hydroxy, hydroxymethyl, carboxy groups) via which crosslinking reactions can be carried out; they may be self-crosslinking or (for example after addition of
35 aminoplastics or epoxy resins) crosslink by external means. The solubility and mechanical properties of

the acrylic resins can be varied widely via the choice of monomers. Cured acrylic resins are generally transparent products which are resistant to UV light and do not discolour.

5

A cold-curing coating resin may have the following composition, for example:

- A) (meth)acrylate from 50 to 100 wt.%
methyl (meth)acrylate from 0 to 5 wt.%
10 ethyl (meth)acrylate from 0 to 5 wt.%
C₃-C₆(meth)acrylate from 0 to 97 wt.%
≥ C₇(meth)acrylate from 0 to 50 wt.%
polyvalent (meth)acrylates from 3 to 10 wt.%
comonomers from 0 to 50 wt.%
15 vinyl aromatic compounds from 0 to 30 wt.%
vinyl esters from 0 to 30 wt.%
the sum of the constituents of components A being 100 wt.%,
- B) from 0 to 2 parts by weight per 1 part by weight
20 of A) of a (pre)polymer that is soluble or swellable in A), the amount of methyl (meth)acrylate or of ethyl (meth)acrylate being > 5 wt.%, based on B,
- C) from 2 to 5 parts by weight per 100 parts by weight of (A+B) of at least one paraffin and/or wax,
- 25 D) a redox system which is to be kept separate, at least in respect of one component of the redox system, until polymerisation of the polymerisable constituents of the system, which redox system contains an accelerator and a peroxidic catalyst or
30 initiator in an amount sufficient for the cold curing of component A), and
- E) conventional additives.

- Mixed resins may be mixtures of polyester resins and vinyl esters and/or acrylic resins in order to achieve

combinations of properties which are particularly advantageous from a commercial point of view.

The resins are mixed carefully with the silica, and the curing agent and, optionally, an accelerator are added thereto. Depending on the curing agent, curing takes place at a temperature which may be markedly below room temperature, in the region of room temperature or in a temperature range markedly above room temperature. The upper temperature limit is generally determined by the physico-chemical data of the resin, such as, for example, the vapour pressure of the monomers.

The duroplastics according to the invention, which contain the structurally modified silica containing acrylic groups, may be liquid, pasty or in solid form.

They may contain: additional pulverulent or fibrous filling materials, such as:

- quartz powder,
- glass fibres,
- pigments,
- flameproofing agents,
- metal oxides,
- metal powders,
- graphite,
- carbon black or
- liquid additives in the form of solvents,
- plasticisers,
- non-reactive extender resins such as hydrocarbon resins,
- resins imparting flexibility, and phenolic resins,
- waxes,
- polymerisation aids and adhesion promoters.

Further additives may be:

- thickeners
- blowing agents,
- mould release agents,
- 5 stabilisers for increasing the useful life.

The silica used in accordance with the invention, which contains methacrylic groups and has been prepared by flame hydrolysis and whose structure has been altered by mechanical after-treatment, brings about a number of
10 technical advantages in the resins according to the invention and preparations prepared therefrom.

In contrast to known finely divided silicas, the thixotropic action is very low. That is of great benefit for the application and loss behaviour of coatings and
15 adhesive preparations.

The acrylic-functional groups firmly bonded to the solid surface react during polymerisation of the reactive resin to form crosslinking sites, which impart to the end product a high degree of hardness, strength and
20 elasticity. In addition, the speed of the crosslinking reaction can be increased, so that coatings are more rapidly dust-dry and laminates can be removed from the mould earlier.

Similarly, the processing of moulding compositions is
25 improved, especially in the case of highly filled systems the reactivity of the silica according to the invention effects uniform through-curing of the moulding within a short time.

A particular advantage when using the silica according to
30 the invention containing methacrylic groups and prepared by flame hydrolysis is also that no free alcohol forms in the preparation, as is unavoidable when using liquid silanes according to the prior art.

The alcohol released on *in situ* silanisation by hydrolysis reaction can give rise to a variety of faults during further processing of the resin preparations, such as acceleration or retardation of the crosslinking process.

- 5 In addition, the silanisation reaction requires a measurable period of time and/or the use of catalysts and/or heat as well as, optionally, measures for removing the alcohol that is formed and excess silane.

- 10 The use in liquid or pasty resins of the silica according to the invention containing methacrylic groups and prepared by flame hydrolysis can have an advantageous effect on the settling behaviour of other fillers, predominantly those having a relatively coarse grain size, even if that effect is not to the fore.

15

Examples

Comparative Example 1:

- 100 parts by weight of an unsaturated, styrene-containing isophthalic acid polyester resin and 1 part by weight of a
20 33 % methyl ethyl ketone peroxide solution in dimethyl phthalate are mixed with the aid of a dissolver. The viscosity is determined at 23°C with the aid of a rheometer. (The viscosity data determined in this and the following Examples are summarised in Table 1). The liquid
25 is then poured into a rectangular steel mould lined with separating foil and heated at 80°C for a period of 15 minutes under a closing pressure of 100 bar. During that time, the composition cures fully and is shaped as a transparent sheet.

30 Comparative Example 2:

- 100 parts by weight of the resin from Comparative Example 1 are mixed with the aid of a dissolver with 15 parts by weight of a silica which is coated with trimethylsilyl groups and has been prepared by flame

hydrolysis and which has a specific surface area of 173 square metres and a carbon content, determined by analysis, of 3.4 wt.%, and whose structure has been altered by mechanical after-treatment. The viscosity is
5 determined at 23°C by brief de-aeration in a low-pressure cabinet. The pasty composition so obtained has a marked flow limit, but is spreadable. 1 wt.% of the 33 % MEK peroxide solution is added thereto, and heating is carried out at 80°C for a period of 15 minutes in a rectangular
10 mould. During that time, the preparation cures fully and is removed from the mould as a translucent sheet.

Example 1 (prior art):

15 parts by weight of a silica which contains methacrylic groups and has been prepared by flame hydrolysis and which
15 has a specific surface area of 160 m²/g, a mean particle size of 12 nanometres and a carbon content of 5 % are mixed with the aid of a dissolver with 100 parts by weight of an unsaturated styrene-containing isophthalic acid polyester resin. The admixed air is removed by brief
20 de-aeration in a low-pressure cabinet. The viscosity is determined at 23°C with the aid of a cone/plate rheometer.

The composition has a flow limit, but is very readily spreadable. 1 wt.% of the 33 % MEK peroxide solution is added thereto, and heating is carried out at 80°C for a
25 period of 15 minutes in a rectangular mould. During that time, the composition cures fully and is removed from the mould as a translucent sheet.

Comparative Example 3 (prior art):

1 wt.% of the 33 % MEK peroxide solution is added as in
30 Example 1 to 100 parts by weight of an unsaturated styrene-containing brominated vinyl ester resin; the mixture is shaped to form a sheet and cured.

Comparative Example 4 (prior art)

100 parts by weight of an unsaturated styrene-containing
35 brominated vinyl ester resin are mixed as in Example 1

with 15 parts by weight of a silica which is coated with trimethylsilyl groups and has been prepared by flame hydrolysis and which has a specific surface area of 173 m² and whose structure has been altered by mechanical after-treatment. The composition is readily flowable.

Example 2 (according to the invention):

15 parts by weight of a silica which contains methacrylic groups and has been prepared by flame hydrolysis and which has a specific surface area of 160 m²/g, a mean particle size of 12 nanometres and a carbon content of 5 %, and whose structure has been altered by mechanical after-treatment, are mixed with 100 parts by weight of an unsaturated styrene-containing brominated vinyl resin. There is no noticeable flow limit, the composition can be poured very readily. It is mixed with 1 wt.% of the 33 % MEK peroxide solution, de-aerated, and shaped to form a sheet and cured as in Example 1.

Comparative Example 5 (prior art):

100 parts by weight of a solution of a PMMA resin in monomeric methyl methacrylate, having the composition:

- a) from 20 to 95 wt.% of a monomeric component composed of
 - a1) from 60 to 100 parts by weight of a (meth)acrylic compound,
 - a2) from 0 to 40 parts by weight of a polyfunctional (meth)acrylate and
 - a3) from 0 to 10 parts by weight of a graft crosslinker,
- b) from 5 to 80 wt.% of a polymer that is soluble in component A), and
- c) from 0.1 to 15 wt.% of a free-radical generator, which already has a low flow limit, are mixed with 3 wt.% of the curing agent, poured out to form a thin sheet and

cured at room temperature. After 15 hours, the sheet has cured through. The surface has a residual tackiness.

Comparative Example 6 (according to the invention):

15 parts by weight of a silica which contains
5 trimethylsilyl groups and has been prepared by
trimethylsilyl flame hydrolysis and which has a specific
surface area of $173 \text{ m}^2/\text{g}$, a mean particle size of 12
nanometres and a carbon content of 3.4 % are mixed with
100 parts by weight of the PMMA resin from Comparative
10 Example 5. The preparation has a markedly increased flow
limit in comparison with Comparative Example 5. It is
mixed with 3 wt.% of the curing agent, poured out to form
a sheet and cured at room temperature. The surface has a
slight residual tackiness.

Example 3 (according to the invention):

100 parts by weight of a PMMA resin from Comparative
Example 5 are mixed intimately by means of a laboratory
dissolver with 15 parts by weight of the silica which
contains methacrylic groups and has been prepared by flame
20 hydrolysis and which has a specific surface area of
 $160 \text{ m}^2/\text{g}$. The flow limit is increased only slightly as
compared with the unfilled resin (Comparative Example 5).
The mixture is then mixed with 3 parts by weight of the
curing agent, poured out to form a thin sheet and cured at
25 room temperature. After 16 hours, the sheet has cured
through. The surface is non-tacky.

Summary of the test results**Table 1:****Properties of the uncured preparations**

	Viscosity, Pas, at 5/s	Thixotropic index 2.5/5	Flow limit upwards Pas
Comparative Example 1	1.34	1	0.2
Comparative Example 2	101.7	1.68	218
Example 1	12.9	1.42	7.6
Comparative Example 3	0.573	1	0.002
Comparative Example 4	95.7	1.77	258
Example 2	2.62	1.13	0.1
Comparative Example 5	8.24	1	40
Comparative Example 6	69	1.65	261
Example 3	23	1.26	65

5 Assessment of Table 1:

Even in the chosen high dosage, the silica containing methacrylic groups and prepared by flame hydrolysis effects a comparatively small increase in viscosity as well as low flow limits of the plastic resin compositions.

10 That property is very advantageous for further processing.

Table 2:
Properties of the cured preparations

	Shore D 10s/60s	Indentation hardness	Tensile strength Mpa	Tensile modulus Mpa	Bending modulus	
Comparative Example 1	78/76	87	47	2367	13853	PE
Comparative Example 2	84/83	106	48	3507	18893	R8200
Example 1	84/83	118	55	4103	23764	R7200
Comparative Example 3	86/85	73	70	4218	23764	VE
Comparative Example 4	85/84	119	50	4960	25213	R8200
Example 2	85/84	121	43	6051	23540	R7200
Comparative Example 5	82/80	101	n.m.	n.m.	n.m.	MMA
Comparative Example 6	83/81	110	n.m.	n.m.	n.m.	R8200
Example 3	85/83	129	n.m.	n.m.	n.m.	R7200

Assessment of Table 2:

As expected, both silicas bring about an increase in
5 hardness and modulus in the crosslinked resin
preparations. In spite of the comparatively lower BET
surface area, the silica modified with methacrylic groups
is distinguished by a substantially more pronounced
action, which leads in Example 2 to a noticeable
10 brittleness of the resin. The person skilled in the art
will recognise the potential for making a saving here and
will reduce the dosage or use a more flexible base resin.

Patent claims:

1. Liquid duroplastics, characterised in that they contain pyrogenically prepared silica which has been surface-modified with silanes containing methacrylic groups.
- 5 2. Liquid duroplastics according to claim 1, characterised in that the pyrogenically prepared silica has been structurally modified.
- 10 3. Method of reinforcing duroplastics, characterised in that a mixture of the uncrosslinked resin and a pyrogenically prepared silica which has been modified with silanes containing methacrylic groups is prepared.

INTERNATIONAL SEARCH REPORT

Application No
PCT/EP 02/07276

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C08K9/00 C08K9/06		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C08K		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the International search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 328 339 A (TIERNEY PAUL A) 27 June 1967 (1967-06-27) column 3, line 18 - line 48; example 1 ---	1-3
X	US 2002/077381 A1 (ETTLINGER MANFRED ET AL) 20 June 2002 (2002-06-20) example 2 ---	1-3
Y	US 2002/077407 A1 (ETTLINGER MANFRED ET AL) 20 June 2002 (2002-06-20) claims 1-7 ---	1-3
Y	US 2002/077388 A1 (ETTLINGER MANFRED ET AL) 20 June 2002 (2002-06-20) claims 1-5 -----	1-3
<div style="display: flex; justify-content: space-between;"> <input type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex. </div>		
<div style="display: flex;"> <div style="flex: 1;"> <p>* Special categories of cited documents :</p> <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document but published on or after the International filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>*&* document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center; font-weight: bold;">16 December 2002</div>		Date of mailing of the international search report <div style="text-align: center; font-weight: bold;">20/01/2003</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer <div style="text-align: center; font-weight: bold;">Marsitzky, D</div>

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